PREPARATION OF THORIA

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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THE PREPARATION OF THORIA.

A Thesis

Presented by

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and

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to the

President and Faculty

of the

Armour Institute of Technology

for the Degree of

Bachelor of Science in Chemical Engineering

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in Chemical Engineering.

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PREFACE.

Reference was made to all technical magazines and works on the chemistry of the rare earths and allied subjects available at the Crerar and Armour Institute libraries. Very little specific information was accessable as seemingly all companies preparing the commercial salt are secretive as to the processes employed. Some very valuable information on magnetic separation, however, was found in an article by Pratt-Sterrett-Hill on "Monazite and Monazite Mining in the Carolinas" in Trans. Am. Inst. Min. Eng. (1909), while Prof. James of New Hampshire College gave us some essential ideas on the sebacic acid separation. All the analyses for thorium were based on the method of Benz in Treadwell's "Quantitative Analysis". To Profs. McCormack, Freud, Tibbals, and Pulsifer we are indebted for many valuable suggestions and for an unflagging interest shown in our work.

TABLE OF CONTENTS.

Preface.	Page.
Introduction.	1.
Part 1.- Preparatory Work.	2.
Chapter 1-General.	3.
Chapter 2-Monazite and Monazite Mining.	4.
Chapter 3-Magnetic Separation.	10.
Chapter 4-Decomposition Methods.	14.
Chapter 5-Precipitants for Thorium.	15.
Part 2.- Experimental Work.	17.
Chapter 1-General.	18.
Chapter 2-Preparation of Sebacic Acid.	19.
Chapter 3-Cleaning.	23.
a-Washing.	23.
b-Screening.	23.
c-Magnetically Separating.	24.
Chapter 4-Digesting and Leeching.	27.
Chapter 5-Purification.	29.
Part 3.- Analytical Work.	34.
Chapter 1-Data.	35.
Chapter 2-Cost Sheet.	36.
Conclusion.	38.

LIST OF ILLUSTRATIONS.

Figure 1.-Sebacic Acid Still. Page 22.

Figure 2.-Magnetic Separator. 26.

INTRODUCTION.

The object of this work is the preparation of commercial thorium oxide by methods economical and at the same time much more rapid than the prevailing processes. The main chance for research seems to lie rather in the separation of thorium from the rare earths than in the decomposition of the mineral. The authors attempted to work on a scale that would yield results directly applicable to the commercial preparation of the salt.

Some difficulty was experienced in getting a sample of desired size, as Brazilian sand was out of the market on account of the war abroad. However, through the courtesy of the Kansas City Mantle Co., we were finally able to get in touch with an old monazite miner, Mr. Hamrick of Bostic, N. C., who supplied us with an adequate sample of washed monazite.

PART 1.

PREPARATORY WORK.

Chapter 1.

General.

This important branch of the work was covered as fully as possible by a thorough search through the literature for useful data. Although the industry is undoubtedly one of decreasing importance, the separation of thorium from the rare earths remains a much discussed topic in the technical literature, and the authors, therefore, feel that they are not working on a subject of past interest only, but rather on one that holds a peculiar fasination for the modern chemist.

Chapter 2.

Monazite and Monazite Mining.

Monazite is essentially an anhydrous phosphate of the rare earth metals, cerium, lanthanum, and didymium- (Ce, La, Di)PO_4, or as written by Prof. Lao, X $Th_3(PO_4)_4$.Y(Ce, La, Nd, -Pr)$_4(PO_4)_4$. There is always present a varying but small percentage of thoria (ThO_2), and silica (SiO_2), which are very probably united in the form of thorium silicate ($ThSiO_4$). The thorium content of the sand will run from 3-7 percent, expressed in terms of the oxide.

Monazite is a light yellow, honey-yellow, reddish, brownish, or greenish yellow, in color, with a resinous to vitreous lustre, and is translucent to subtransparent. It is brittle with a concoidal to uneven fracture, and is from 4.64- 5.30 in specific gravity. It crystallizes in the monoclinic system, and some crystals have been observed that were 6 inches in

length. The more perfect crystals are, however, very small, ranging in length from .5 inch down to microscopic sizes. The principal chemical and blowpipe reactions that can be readily employed to identify monazite are the following: it is incompletely soluble in hydrochloric acid, but it completely and readily acted upon by sulphuric acid. If oxalic acid is added to a very dilute, filtered, sulphuric acid solution, or to the acid solution obtained by fusing the mineral with soda, a precipitate is obtained which, upon ignition, becomes brick red, due to the presence of cerium oxide. Before the blowpipe the mineral turns grey, but is infusible. If heated with sulphuric acid, it colors the flame bluish green, due to the phosphoric acid.

Monazite has been found in several varieties of rocks, in soils derived from monazite bearing formations, and in gravel beds formed through the erosion of these formations. Only gravel deposits have been worked profitably

for monazite on an extensive scale, though in some places the surface-soils adjoining rich deposits of monazite, or the sapolite or rotted rock underlying them, are found to be sufficiently rich in monazite to be sluiced down and washed. Commercial deposits occur in gravel beds of creeks and streams and also in sea-sands. The thickness of the gravel varies from 1-8 feet. The sand is much richer near the bed rock. Gravel deposits contain about 1 percent monazite and are concentrated by washing. The monazite is fed by hand into sluice boxes, these being fitted at the upper end with a sieve or shaking hopper, with a mesh about number 12. The boxes vary in length from 5-20 feet, and in some instances are fitted with riffles holding mercury for catching gold. A washed gravel bed will be ready for another washing in about a year if there has been much rain.

In a few places, Wilfley tables have been introduced for treating the concentrates from

the sluice boxes. Where these tables are used the soil and gravel are washed into shaking hoppers and then through sluice boxes, the over size thrown out, and the sands fed to the Wilfley tables. At one mine it is necessary to raise the gravels by a mech anical elevator in order to bring them to a sufficient height to feed them to the table. They are fed into revolving screens and then to the tables. The heads from the first washing do not contain a very large content of the monazite, and the middlings are, therefore, re-fed to the tables with other feed-ore. In some cases the feed-ore is all run over the machine and a rough concentrate first obtained and then re-fed. The product from these machines contains from 30-70 and occasionally 80 percent monazite. Where there is a large amount of the heavy, black; sands occuring in the gravel with the monazite, it is almost impossible to get the monazite much more than 30 percent pure.

All the concentrates from the sluice

boxes and the Wilfley tables have to be dried before they can be treated on the magnetic separators. The two following methods are used for drying:

(1)- By solar heat.

The sand is spread over an oiled or rubber-covered cloth in a thin layer and exposed to the heat of the sun. It dries very quickly due perhaps partly to the heat absorbed by the dark iron sand.

(2)- By furnace heat.

A small ditch, from 1.5-2 feet wide and 1 foot deep, is dug, at one end of which there is built a rock or brick chimney. The ditch is usually built up of stones with an opening at the end opposite the chimney for firing. Over the ditch there is a sheet-iron cover or drying plate. The monazite is spread on this plate and exposed to the action of the hot fire underneath.

The dried sands are occasionally further concentrated by means of the ordinary horse-

shoe magnet, which picks out all of the magnetite. The miners are paid for the sand on the basis of 100 percent of the product, and the higher the concentration, the better the price they recieve. The sand bought in the magnetic-concentration plants is worth from 4-8 cents per pound, while after concentration with electro-magnets, the price reaches about 12 cents per pound.

Chapter 3.

Magnetic Separation.

In order to separate the monazite from its associated minerals, it is necessary to run the sand through some electrical appararus. By means of electro-magnetic separators, it is possible to obtain a product varying from 90-98 percent monazite. Electro-magnets are usually used instead of permanent steel magnets, since they give a greater and more constant flux. The magnetism of the electro-magnet can be varied and different intensities obtained, ranging from infinitely weak to a certain maximum strength. It is also possible to control the intensity of any magnetic field, so that the minerals that are strongly attracted may be separated from the minerals that require a magnetic field of higher intensity. The intesity of the magnetic field depends on the four following facts:

(1)- On the size of the magnet.

(2)- On the shape of the magnet.

(3)- On the distance between the magnet and the body to be attracted.

(4)- On the number of ampere turns in the magnet coils.

There are three general types of magnetic separators:

(1)- The Wetherill separator.

This separator embraces that type in which the magnetic particles are carried by conveying belts or pans passing over the magnets. The machine consists of two conveyor belts at right angles. The material to be separated is fed on the lower belt, and as it goes along, the cross belt with a strong electromagnet suspended above it, draws off the magnetic material and lets it drop in the tailings, while the cleaned sand falls in a separate compartment.

(2)- The Ball-Norton separator.

This consists of two revolving drums,

within each of which is a series of stationary magnets. The material is fed to the drums usually from a hopper. As soon as it touches the drums, the magnetic material will be pulled away and carried 180 degrees by the drum and dropped in the tailings, while the non-magnetic material falls in the heads.

(3)- The Edison separator.

In this separator the particles of the mineral are permitted to fall in a thin sheet in front of the poles of a strong bar or horse-shoe electro-magnet, which causes a deflection of the magnetic particles from a direct downward path, while the non-magnetic particles are not influenced by this attraction and fall vertically. It is possible to make two and sometimes three products in this way. In many instances it is found advantageous to wet the mineral to be separated before feeding it to the machine. It is possible to operate with direct or alternating current. By increasing the current for each run, magnetite, ilmenite,

chromite, and garnet, may be conviently separated from the monazite sand.

The following table shows the relative amperes sent through a magnet of many turns to clean monazite sand:

Amperes	Substance Removed.
.2	Magnetite.
1.1	Ilmemite.
1.6	Chromite.
1.75	Garnet.
2.2	Olivine.
3.5	Monazite.

Chapter 4.

Decomposition Methods.

The following four methods for the decomposition of the sand were considered, but only the first was found at all practicable.

(1)- Sulphuric acid digestion.

The digestion of finely ground monazite from 8-12 hours in concentrated sulphuric acid and the subsequent leeching of the soluble sulphates from the insoluble material.

(2)- Thorium carbide method.

The following charge treated in an electric furnace for 1.5 hours at 35 volts and 25 amperes to form thorium carbide:

Monazite ------1 pound.

Petroleum coke-1.1 pounds.

Lime ---------- .8 pounds.

Fluospar------- .15 pounds.

(3)- Alkaline fusion in electric furnace.

(4)- Sublimation of thorium carbide.

Chapter 5.

Precipitants for Thorium.

The following precipitants for thorium in the presence of the rare earths were found in the course of the library work.

(1)- Chlorine on the suspended hydroxide.

(2)- Potassium permanganate.

(3)- Hydrogen or sodium peroxide.

(4)- Fractional precipitation with ammonium hydroxide.

(5)- Partial precipitation with analine.

(6)- Fractional precipitation with sodium or potassium hydroxide.

(7)- Precipitation with alkali hyponitrites.

(8)- Precipitation as the chromate.

(9)- Fractional crystallization of the double salts.

(10)-Precipitation with sebacic acid.

(11)-Precipitation with potassium stearate.

(12)-Formation of basic nitrates, chlorides,

or sulphates.

(13)-Electric current.

Of the above, the only two methods that seemed at all industrially possible were the separations with sebacic acid and hydrogen peroxide.

PART 2.

EXPERIMENTAL WORK.

Chapter 1.

General.

The sulphuric acid decomposition method recommended itself more strongly to the writers than the other three, as these latter demanded an electric furnace equipment, the expense of which seemed all out of proportion to its utility.

Of the many quantitative precipitants known for the separation of thorium from the rare earths, the authors chose hydrogen peroxide and sebacic acid, these being of all suggested, the most rapid and economical.

On a large scale no doubt, the Wetherill magnetic separator is to be preferred, but under existing circumstances, the Edison process was used.

Chapter 2.

Preparation of Reagent-

Sebacic Acid.

Owing to the cessation of imports from Germany, it was found necessary to prepare our own sebacic acid. It was here, perhaps, that the writers met with their greatest disappointment, as the yield was far from satisfactory. Enough of the acid was prepared, however, to run a test precipitation on an aliquot portion of the rare earth solution.

The acid was prepared in the following manner:- The set up was as shown in the figure, the retort being of cast iron, with the clamped cover drilled for a thermometer and a condenser lead. The vacuum was applied at the receiver end as indicated, the receiver being a heavy glass filter flask. The receiver connection was made of asbestos packing, which was found very satisfactory. The system was

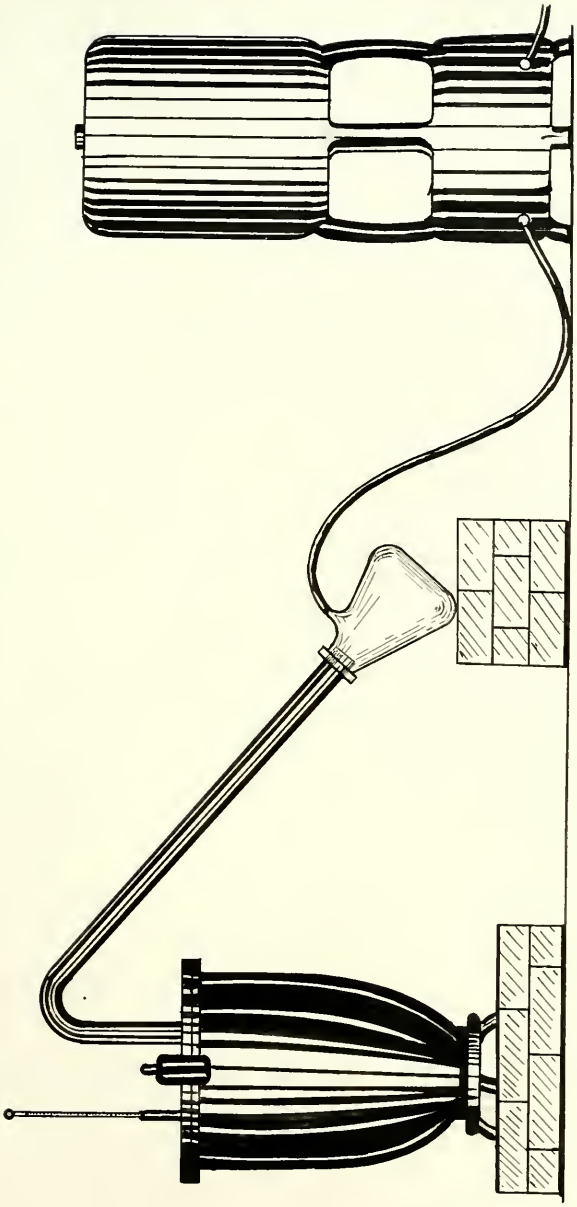
kept under a vacuum by an impeller type fan, driven by a 110 volt, 2.6 ampere motor. As for the high vacuum necessary the motor was somewhat overloaded, a fan was used to keep down the temperature of the machine.

Sodium oleate was the raw product employed. Five pounds of commercial oleic acid was saponified with the calculated amount of commercial sodium hydroxide, the operation being completed in a boiling kettle and the soap being"salted out"with sodium carbonate. After drying, the resultant product was ready for distillation, this being accomplished in three runs. The conditions which gave a maximum yield were a vacuum of 28 inches and a temperature of 270°C. The acid appeared in the receiver as a white floculent solid on the top of the other decomposition products. The distillate from the three runs was collected and the sebacic acid separated. This was then carefully dried, the yield being 40 grams.

The reaction may be expressed as:-

$C_{17}H_{33}(COONa) + \Delta^{o} = C_{8}H_{16}(COOH)_{2}$ + other products.

(sodium oleate) (sebacic acid)



Chapter 3.

Cleaning.

Washing.

The sand as delivered had been thoroughly washed, so thoroughly perhaps that much of the fine monazite had been washed away with the sand, as otherwise the high percentage of large garnets and the low percentage of thoria is almost unaccountable.

Screening.

Screening was the next operation, this being conducted by the authors. The monazite was run through a hand screen of one millemeter mesh, which operation removed in large part the garnets and also some of the magnetite.

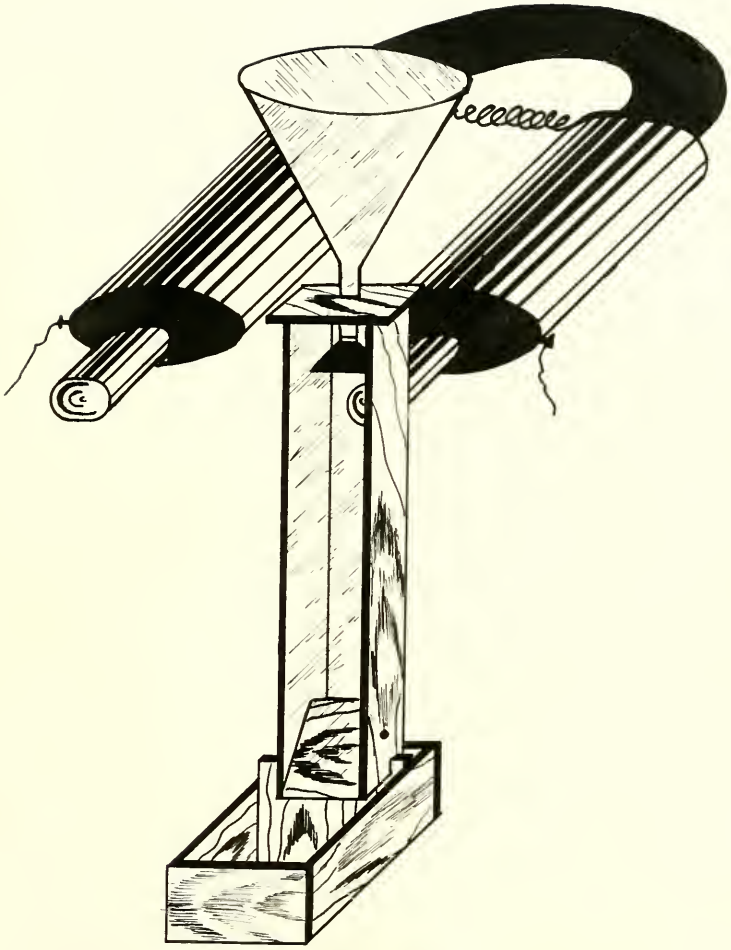
Magnetically Separating.

As previously stated, the method chosen was that perfected by Edison and is shown in the following diagram. The separator, which was placed as shown, was a small rectangular tower,

the two faces directly in the field being of glass, and the other two of wood. Near the bottom and with its axis perpendicular to the field, was a wooden wedge, with width that of the tower, and with an edge facing upwards. Its position was easily controlable, and thus served as a simple means for separating the deflected from the undeflected particles. The monazite was fed from a glass funnel hopper, provided with a "spreader feed". The electro-magnet used was of the horse-shoe type, with 20,000 turns, and capable of carrying a current of 40 amperes. The magnet was connected to a generator circuit of 25 amperes under 110 volts.

The monazite was fed in the tower rather rapidly, the magnetite and hematite being collected on the side nearest the magnet and the less magnetic material being allowed to fall into the opposite compartment. This latter material was then run through the tower a second time, under such an increased flux that not only was

the remainder of the ferrous material removed, but also some of the minerals lying in the permeability scale between ferrite and monazite.



Chapter 4.

Digesting and Leaching.

Digesting.

The cleaned monazite was passed through rolls adjusted to grind to 50 mesh and was then decomposed with concentrated sulphuric acid. For this two enameled pots, each about 8 pounds sand capacity, were used. To each monazite charge, an equal weight of concentrated sulphuric acid was added and the digestion continued with frequent stirring until complete decomposition, this requiring from 10-12 hours. At the end of this time, the rare earths were completely in solutions as sulphates, while the calcium as calcium sulphate and the silica as gangue were largely left as a heavy grayish residue. In all, 50 pounds of the bolted monazite were thus treated.

Leaching.

To the combined solutions and residue, water was added to about three times the bulk

of the digested material. The whole was frequently stirred, and after settling overnight, the supernatant liquid was siphoned off and a fresh and equal portion of water added. This was repeated several times, until on the fourth leaching but slight amounts of the rare earths were found in solution. The solutions were then mixed and poured into precipitation jars.

Chapter 5.

Purification and Crystallization.

With the addition of ammonium hydroxide to near neutrality, the metallic radicals present were precipitated from solution as phosphates, in the form of a heavy, white crystalline powder. This was bag-filtered and washed free of sulphuric acid with water. The phosphates were dissolved, and from the solution, after making as neutral as possible with ammonium hydroxide with the formation of a permanent precipitate, the rare earth oxalates were precipitated by the addition of a slight excess of a hot concentrated solution of oxalic acid. This was allowed to stand over night, when, after decanting the clear liquor, the wet precipitate was filtered and dried in an oven. Contrary to all information as found repeatedly in the literature, the rare earth oxalates are practically insoluable in concentrated nitric

acid. It was, therefore, found necessary to decompose the oxalate, which was first powdered, in sulphuric acid, and to take almost to dryness in order to decompose all free oxalic acid. This was an extended operation, requiring from 2-3 days.

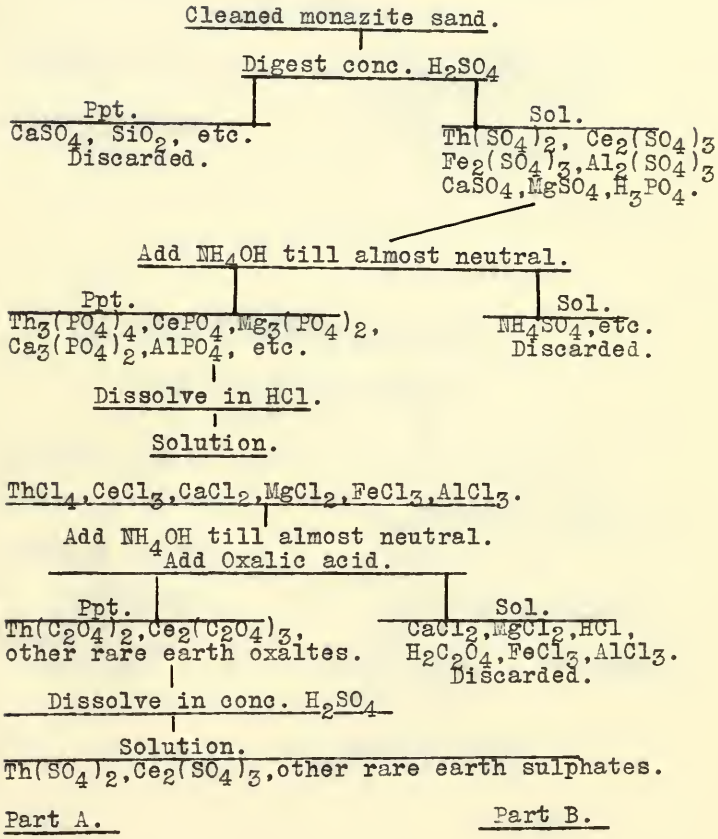
On heating the residue with dilute sulphuric acid, a clear solution of the rare earth sulphates was obtained. To one portion of this solution, ammonia was added until the precipitated hydroxide barely redissolved. Hydrogen peroxide in small calculated excess was added to the hot solution, (about 70°C), this precipitating all of the thorium and but a small part of the rare earths as the peroxide, this precipitate being immediately filtered. This was reduced over a rose burner to the oxide, and sample-bottled as commercial thoria.

The balance of the sulphate solution, comprising but a small part of the whole, was then neutralized as above and heated to boiling. To this a boiling solution of sebacic

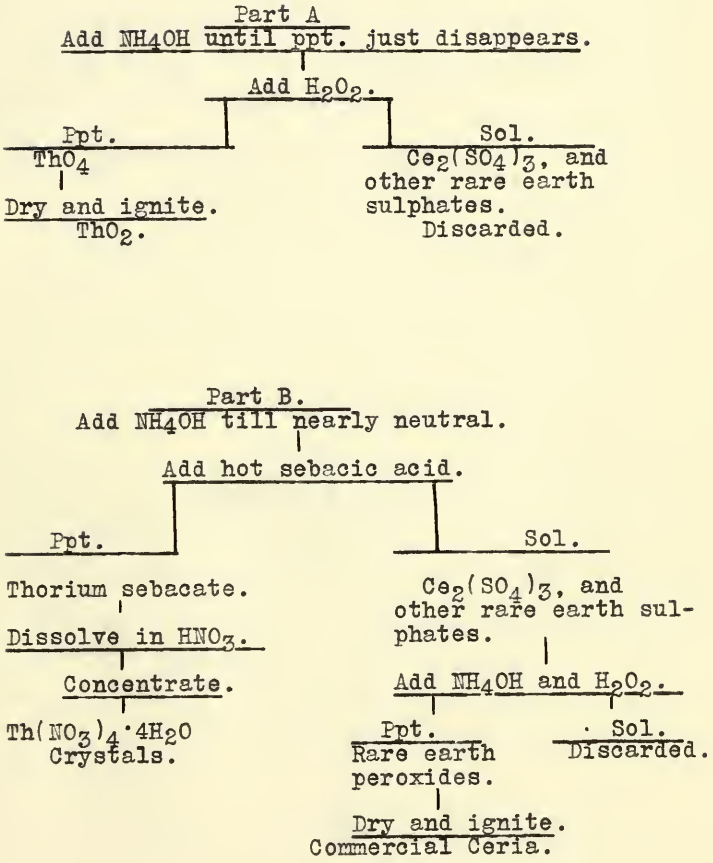
acid, (40 grams in 200 cubic centimeters of water), was added with constant stirring, to give a white rapid-settling precipitate of thorium sebacate. This was filtered, washed with boiling water, and dissolved in dilute nitric acid. The nitrate solution was then concentrated to incipient crystallization; subsequent cooling giving the pure thorium nitrate crystals of the formula, $Th(NO_3)_4 \cdot 4H_2O$.

To the filtrate from the peroxide precipitation, additional quantities of peroxide and ammonia were added with the formation of cerium, lanthanum, and didymium peroxides, which were filtered, dried, and ignited to commercial cerium oxide.

SCHEME OF PROCEDURE.



SCHEME (CONT.).


Part A
Add NH_4OH until ppt. just disappears.
Add H_2O_2.
Ppt.
ThO_4
Dry and ignite.
ThO_2.
Sol.
$Ce_2(SO_4)_3$, and other rare earth sulphates.
Discarded.
Part B.
Add NH_4OH till nearly neutral.
Add hot sebacic acid.
Ppt.
Thorium sebacate.
Dissolve in HNO_3.
Concentrate.
$Th(NO_3)_4 \cdot 4H_2O$ Crystals.
Sol.
$Ce_2(SO_4)_3$, and other rare earth sulphates.
Add NH_4OH and H_2O_2.
Ppt.
Rare earth peroxides.
Dry and ignite.
Commercial Ceria.
Sol.
Discarded.

PART 3.

ANALYTICAL WORK.

Chapter 1.

Data.

Analysis of Monazite Sand.

(From the farm of J.M.Hamrick,Bostic,N.C.)

Sample-	No.1	No.2	No.3	No.4
ThO_2-	2.73%	2.58%	2.41%	3.04%
Ce_2O_3,etc.-	41.21"	41.87"		
CaO-	4.96"	4.82"		
MgO-	1.08"	1.14"		
Fe_2O_3-	13.35"	13.26"		
Al_2O_3-	11.64"	11.75"		
SiO_2-	1.41"	1.49"		
P_2O_5-	25.46"	25.26"		

Cleaning.

Used 50 Pounds Monazite Sand.

Removed by-

Screening ---------- 5.6 lbs. garnets,etc.

Magnetic separation-

4.1 lbs. Fe_2O_3,FeO.
.3 " garnets, etc.
10.0

Net amount of cleaned monazite = 40.0 lbs.

Yield.

Thoria ---------- .96 lbs.

Thorium nitrate- 40 gms. = .048 lbs. oxide.
Total yield = 1.008 lbs. ThO_2.

Percentage recovery.

Possible recovery of thoria- 1.345 lbs.

Actual recovery of thoria--- 1.008 Lbs.

Percentage recovery--------- 74.93%.

Analysis of Thoria.

$Th(NO_3)_4 \cdot 4H_2O$ (weighed as ThO_2)-- 98.75%.

Chapter 2.

Cost Sheet.

Cost of Chemicals Used.

54 lbs. H_2SO_4 at $.06 per lb. ---- $3.24

20 lbs. NH_4OH at $.07 per lb. ---- 1.40

14 lbs. HCl at $.06 per lb. ---- .84

8 lbs. $H_2C_2O_4$ at $.15 per lb. ---- 1.20

4 lbs. H_2O_2 (15%) at $.60 lb. ---- 2.40

5 lbs. Oleic acid at $.08 lb. --- .40

Total = $9.48

Cost of Monazite Sand.

50 lbs. monazite sand at $.12 lb.- $6.00

Total cost=$15.48

Cost of thoria as extracted (materials only)-

$15.48 per lb.

Worth at market($9.50 per lb. as nitrate)-

$19.40 per lb.

CONCLUSION.

As is the case with so many laboratory tests attempted on a semi-commercial scale, the results obtained were hardly illuminating as to actual cost data. The cost of both chemicals and raw product was undoubtedly all out of proportion to that obtaining in the manufacturies. One reason, of course, for the poor economy of the process was the fact that no recovery of the by-products ceria, rutile, iron sulphate, oxalates, garnets, and etc., was attempted, whereas in actual practice, many or all of these side products are recovered.

The work has perhaps been of value, however, as the authors believe that the use of hydrogen peroxide has been proven commercially practicable, while it is believed that the successful use of sebacic acid has been shown improbable.

Under prevailing conditions, that is to say, with the price of thorium salts advanced three hundred percent above normal, it is possible even with the high costs obtained, to

manufacture and sell the commercial salt at a profit. It is evident, however, from the experimental data, that under normal conditions, a full use must necessarily be made of all by-products, while all other fixed charges must be kept at a minimum.